Part 4- Session Presentations for the EPA 23rd Annual National Conference on Managing Environmental Quality Systems

April 13-16, 2004   Tampa, Florida

NELAC I

NELAC II

Use of Proficiency Testing Data to Identify Systemic Problems in Environmental Data (Chuck Wibby, Wibby Environmental)

Building EPA's Analytical Capabilities

Training Environmental Statisticians, Tomorrow's Problem Solvers (Bill Hunt, North Carolina State University)

New SAS Users Group at EPA and SAS Enterprise Guide Software at EPA (William Wallace, U.S. EPA)

Building Analytic Capability at EPA: What Can SAS Contribute? (Catherine Truxillo, SAS)

Effluent Guidelines and Testing

Continuous Improvement and Validation of EPA Method 1668A Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids and Tissue by HRGC/HRMS (William Telliard, U.S. EPA)

A New Tool to Support the Quality of the Clean Water Act's (CWA's) Whole Effluent Toxicity Testing Programs under the Clean Water Act (Marion Kelly, U.S. EPA)

Application of the Effluent Guidelines Data System for Review of Primary Data (William Telliard, U.S. EPA)

NCSU Student Projects and Perspectives

William F. Hunt, Jr.
Visiting Senior Scientist
&
Dr. Kimberly Weems
Teaching Assistant Professor

NSF NCSU/Spelman College Collaborative Effort: Environmental Statistics Practicum

NCSU
William F. Hunt, Jr.
Dr. Kimberly Weems
Michael Crotty

Spelman College
Dr. Nagambal Shah
Dr. Monica Stephens

EPA Region 4
Van Shrieves

Georgia DNR
Susan Zimmer- Dauphinee

NCSU Clients

- Dr. Ellis Cowling, Director of the **Southern Oxidant Study at NCSU**
- Dr. Kenneth Schere and Mr. David Mobley of the **USEPA, Office of Research and Development**
- Mr. Fred Thompson, Mr. Neil Frank, Dr. Conniesue Oldham, Mr. Fred Dimmick, Mr. David Mintz, Mr. William Cox and Mrs. Barbara Parzygnat, **USEPA's Office of Air Quality Planning and Standards**

Clients Continued

- Mr. George Murray, Mr. Hoke Kimball, Mr. Steve Few, Mr. John White, Ms. Harvi Cooper and Mr. Pat Bello of the **North Carolina Department of Environment and Natural Resources** (NCDENR)
- Mr. Lewis Weinstock and Mr. Pat Reagan of the **Air Monitoring Division of the Forsyth County Environmental Affairs Department**
- Mrs. Claire Huson and Mr. Ken Doolan of the **U. S. Department of State**

Clients Continued

- Mr. Tom Furmanczyk and Mr. Tom Dann of **Environment Canada**
- Dr. Cyril Durrenberger, **University of Texas**, Austin, TX
- Ms. Candy Garrett and Mr. Erik Gribbin, **Texas Commission on Environmental Quality**, Austin, TX

Professional & EPA Technical Meetings & Undergraduate Research Symposia

- **Southern Oxidant Study Data Analysis Workshop,** Research Triangle Park, NC, March 9, 2000;
- **NCSU Undergraduate Research Symposium,** McKimmon Center, Raleigh, NC, April 27, 2000;
- **USEPA Technical Workshop on PM 2.5 Monitoring, Quality Assurance, and Data Analysis**, Cary, NC, May 22-25, 2000;
- **Future Directions in Air Quality Research, Ecological, Atmospheric, Regulatory/Policy and Educational Issues**, Research Triangle Park, NC February 12, 2001;
- **NCSU Undergraduate Research Symposium**, McKimmon Center, Raleigh, NC, April 19, 2001;
- **NC Department of Environment and Natural Resources Data Analysis Colloquium**, Raleigh, NC, May 23, 2001.

Professional & EPA Technical Meetings & Undergraduate Research Symposia

- **Second Annual NC State University Minority Graduate Education (MGE) Summer Research Program Poster Session**, July 23, 2001.
- **Mathfest 2001, sponsored by Mathematical Association of America and Pi Mu Epsilon**, Madison, Wisconsin, August 2-3, 2001.
- **2001 Sigma Xi Student Research Symposium**, Raleigh, North Carolina on November 10, 2001.
- **NCSU Undergraduate Research Symposium**, Raleigh, NC, April 18, 2002.
- **North Carolina Department of Environment and Natural Resources Data Analysis Colloquium**, Raleigh, NC, May 23, 2002.

Professional & EPA Technical Meetings & Undergraduate Research Symposia

- **First Annual NC State Undergraduate Summer Research Program Symposium**, August 9, 2002.
- **Joint Statistical Meetings**, New York City, New York, August 11 - 15, 2002.
- **Air & Waste Management Association's Annual South Atlantic States Section Meeting**, Research Triangle Park, NC, December 4, 2002.
- **NCSU Undergraduate Research Symposium**, McKimmon Center, Raleigh, NC, April 10, 2003.
- **NC Depart. of Environment & Natural Resources Data Analysis Colloquium**, Raleigh, NC, May 23, 2003.
- **96th Annual Air & Waste Management Association Meeting**, San Diego from June 22-26, 2003.

Student Awards

- D. R. Harrington, **"Protecting the Public Health – Forecasting Photochemical Air Pollution in Charlotte, NC."** NCSU Undergraduate Res. Symposium, April, 27, 2000. **CASH AWARD**
- Jason Grissom, **Comparison of Particulate Matter Levels in Worldwide Megacities,** report prepared for, US State Dept., August 17, 2000. **(USA Today Award)**
- Kathy Woodside, **"Protecting the Public Health: Forecasting Fine Particular Matter in Forsyth County."** Mathfest 2001, Mathematical Association of America & Pi Mu Epsilon, Madison, WI, August 2-3, 2001. **CASH AWARD for Best Talk**
- Darious Brooker, Ho Ling Cheng and Jeffrey Thomas, **Undergraduate Research Award for $2000** to pursue their research on the USEPA's Toxic Research Inventory.

Student Awards

- Tracy Robinson, "Saving the Earth by Reducing Ground Level Ozone: What Can We Learn by Examining the Atlanta Ozone Precursor Data?" **NCSU Undergraduate Research Symposium**, Raleigh, NC, Apr. 18, 2002. **CASH AWARD**
- Karen Donaghy and Courtney Sorrell, "Designing Models to Predict Tomorrow's Air Pollution." **1st Ann. NC State Undergraduate Summer Research Symposium, August 9, 2002. AWARD**
- Karen Donaghy and Courtney Sorrell won the **Undergraduate Research Award for $2000** each to pursue their research on Predicting Tomorrow's Air Pollution, November 27, 2002 .
- Karen Donaghy and Courtney Sorrell, "Designing Models to Predict Tomorrow's Air Pollution." **Air & Waste Management Association's Annual South Atlantic States Section Meeting, December 4, 2002. Won 3rd prize.**
- Karen Donaghy and Courtney Sorrell, "Improving the Forecast for Tomorrow's Air Pollution." **NCSU Undergraduate Research Symposium, McKimmon Center, Raleigh, NC, April 10, 2003. Both students won the $200 cash prize for poster.**

Student Awards

- **Caleb Rowe and Valerie Harris**, "A Tale of Three Cities – How Does Urban Growth Impact Air Pollution? Second Annual NC State Undergraduate Summer Research Symposium, Raleigh, NC. August 9, 2003. **Received an Award.**
- **Louise Camalier, Brendan Yoshimoto and Brian Stines** won the **Undergraduate Research Award for $500** each for their project, "Solving the Houston Air Quality Emission Inventory Discrepancy - Expanded Statistical Methodology Applications to Atlanta, GA," on November 18, 2003.
- **Ornella Darlington-Turner and Brian Currier** won the **Undergraduate Research Award for $500** each for their project, "Water Quality Trends in the Raleigh-Durham Metropolitan Area" on November 18, 2003.
- **Jamie Ridenhour and Jennifer Lawhorn** won the **Undergraduate Research Award for $500** each for their project, A Statistical Model to Forecast Fine Particulate Matter Air in Charlotte, NC" on November 18, 2003.

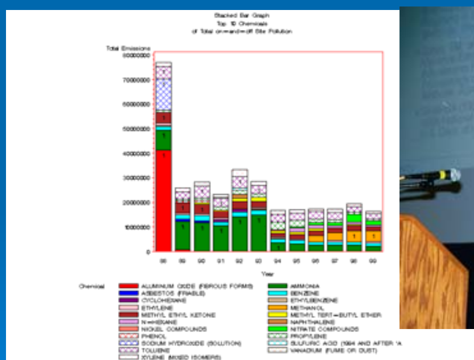
Jason Grissom, **Comparison of Particulate Matter Levels in Worldwide Megacities,** report prepared for, US State Dept., August 17, 2000. **(USA Today Award)**

Table 3. Comparison of TSP, estimated $PM_{2.5}$ annual mean statistics in worldwide cities.

City	TSP Mean Conc.	Est. $PM_{2.5}$ Mean	Ratio of $PM_{2.5}$ Mean to annual NAAQS
Barcelona	117	36.9	2.46
Bogota	120	37.8	2.52
Rio de Janeiro	139	43.8	2.92
Quito	175	55.2	3.68
Athens	178	56.1	3.74
Sofia	195	61.4	4.09
Manila	200	63.1	4.20
Bangkok	223	70.3	4.69
Bombay	240	75.7	5.04
Shanghai	246	77.5	5.17
Jakarta	271	85.4	5.69
Mexico City	**279**	**87.9**	**5.86**
Chengdu	366	115.4	7.69
Shenyang	374	117.9	7.86
Calcutta	375	118.2	7.88
Beijing	377	118.9	7.93
New Delhi	415	130.8	8.72

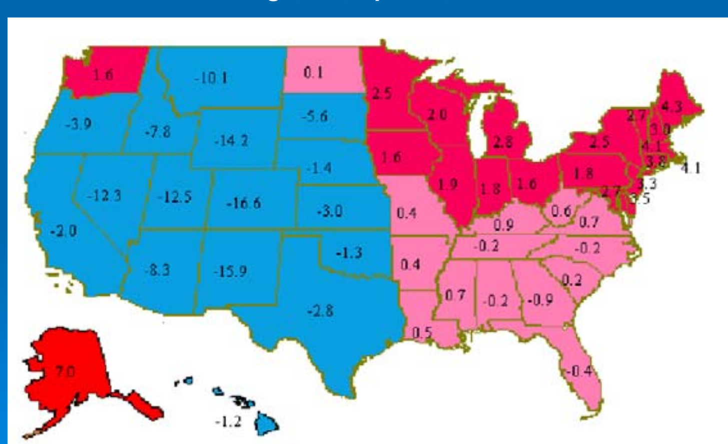
Can Toxic Release Trends in the Petroleum Industry be Explained? Jeffrey A. Thomas, Darious J. Brooker & Ho-Ling Cheng

$2000 Each Undergraduate Research Award



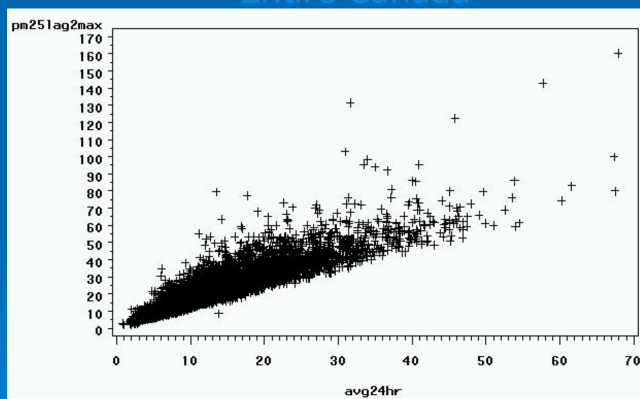
Brian Copeland, "Standard Conditions of Temperature and Pressure vs. Local Conditions - What does it mean for air pollution control?"

NCSU Undergraduate Research Symposium, McKimmon Center, Raleigh, NC, April 19, 2001.



Leslie Schnell, Amy Gabig and Brian Spruell, "Protecting the Public Health – Developing Hourly Air Quality Standards for Environment Canada and the US."
NCSU Undergraduate Research Symposium, McKimmon Center, Raleigh, NC, April 18, 2002.

Entire Canada



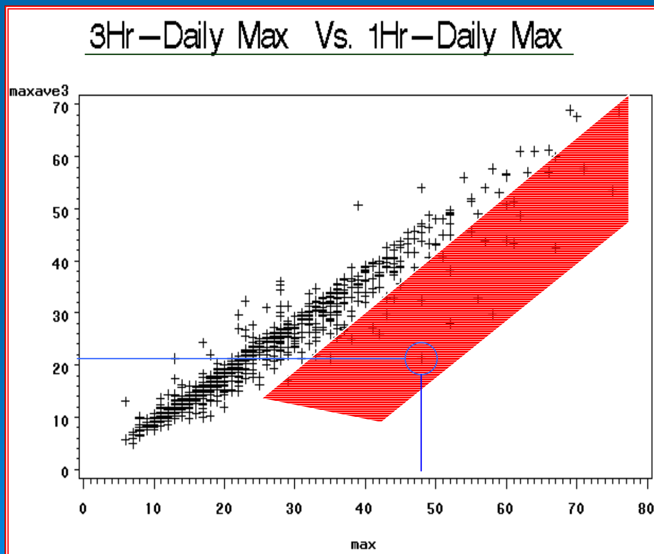
R=.89872(.8077)

"An Examination of a Possible Short Term Hourly Standard for PM Fine."

Benjamin Ogorek

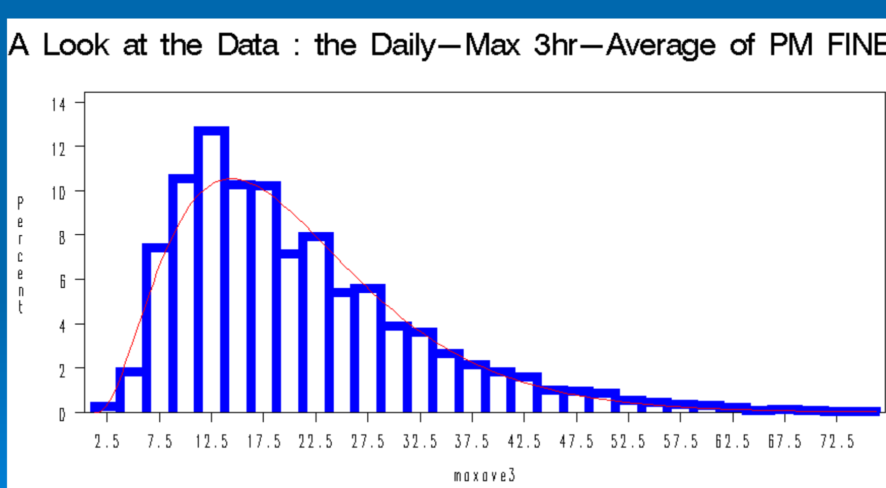
96th Annual Air & Waste Management Association Meeting, San Diego from June 22-26, 2003

But … Why Not a 1Hr Max?

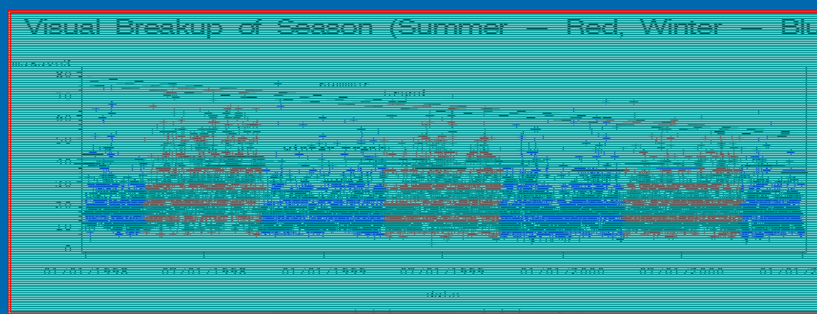


Many runaway 1-hour observations cause this statistic to violate standards when in fact the PM concentrations are under control.

Gamma Fit?



A Possible Summer Trend?



Summers *alone* are experiencing a negative trend.

Temporary? … Coincidence??

Leads to Joint Paper

An Alternative PM Fine Standard, Based Upon the Daily Max Hour PM fine Value

William F. Hunt, Jr., Dr. Kimberly Weems and Benjamin Ogorek

Department of Statistics

North Carolina State University

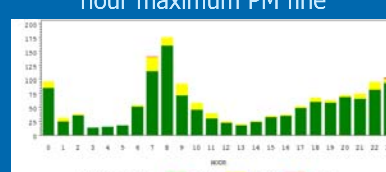
Karen Donaghy and Courtney Sorrell

- “Designing Models to Predict Tomorrow’s Air Pollution.” **1st Ann. NC State Undergraduate Summer Research Symposium, August 9, 2002.** **AWARD**
- Both won the **Undergraduate Research Award for $2000** each to pursue their research on Predicting Tomorrow’s Air Pollution, November 27, 2002 .
- “Designing Models to Predict Tomorrow’s Air Pollution.” **Air & Waste Management Association’s Annual South Atlantic States Section Meeting, December 4, 2002.** **Won 3rd prize.**
- “Improving the Forecast for Tomorrow’s Air Pollution.” **NCSU Undergraduate Research Symposium, McKimmon Center, Raleigh, NC, April 10, 2003.** **Both students won the $200 cash prize for poster.**

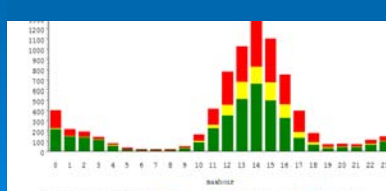
PM, Ozone, and CO

Diurnal Pattern of summer daily one hour maximum PM fine

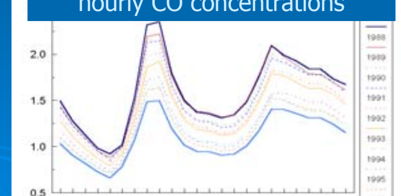
Diurnal Pattern of winter daily one hour maximum PM fine



Summer Diurnal Pattern of Ozone



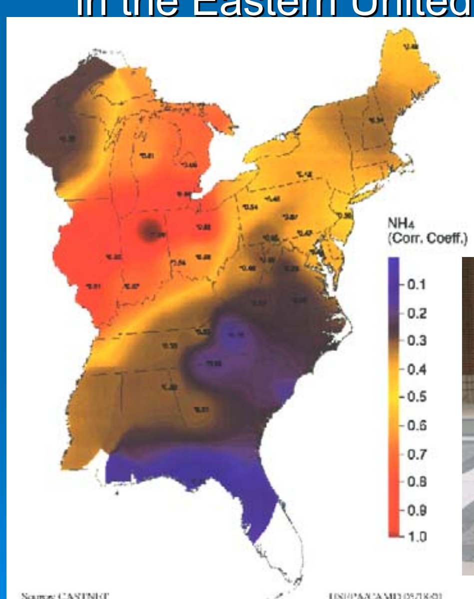
Diurnal Pattern of mean winter hourly CO concentrations



Alan Shoulders, Hampton University Summer 2002 - Data we have so far… (Morning Averages)

Atlanta and Charlotte	Benzene	Toluene	M&P Xylene	O-Xylene	Acetylene
South Dekalb	3.09315	11.8396	6.08995	2.36634	2.29447
Conyers	1.31618	4.2379	2.01683	0.77217	0.90676
Tucker	3.28853	11.8426	7.00279	2.46414	1.93565
Yorkville	0.46961	1.5019	0.58188	0.14572	0.35302
Plaza	6.36945	17.1967	10.0580	3.78818	10.0343
Enochville	2.48195	7.0644	3.1062	1.27516	4.9708

Spatial and Temporal Analysis of Ammonium in the Eastern United States, 1990-99

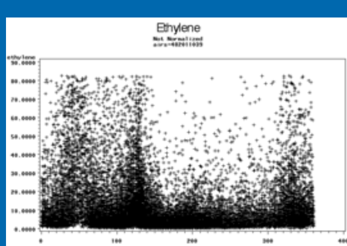


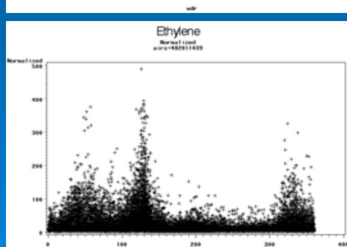
Eliza J. Britt, KeTrena Langhurst, and Jiaomei Liu

"Resolving the Volatile Organic Compound to Nitrogen Oxides Discrepancy in Houston."

- **NCSU Undergraduate Research Symposium, McKimmon Center, Raleigh, NC, April 10, 2003.**
- **96th Annual Air & Waste Management Association Meeting,** San Diego from June 22-26, 2003.

Why and How We Normalized the Data!!





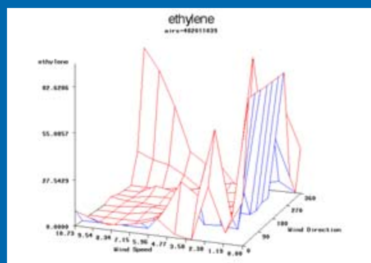
Screen3, a single source Gaussian plume model, was used to normalize the data. The details of this model can be found at the following website:
http://www.epa.gov/scram001/tt22.htm#screen3

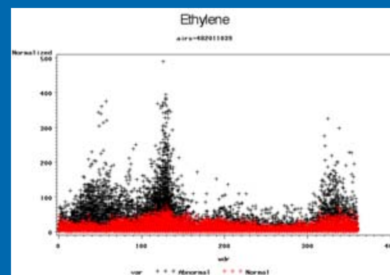
From the Screen3 model, we know that the concentration is equal to emissions/(wind speed*sigma z*sigma y). Wind speed tends to be more variable than that of the sigmas. Resulting in the following formula:

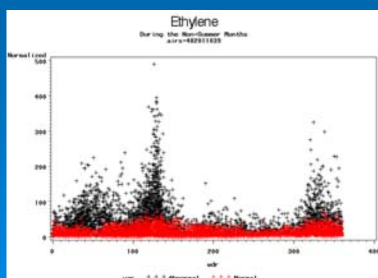
Normalized = Concentration*Wind Speed

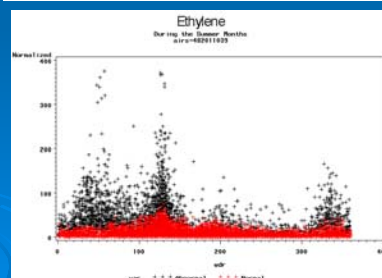
Patterns appeared in the data after the VOC was normalized. An example of emerging patterns can be seen in the before (top) and after (bottom) normalization plots.

Ethylene at the Deer Park Site: How the Wind Affects the Data



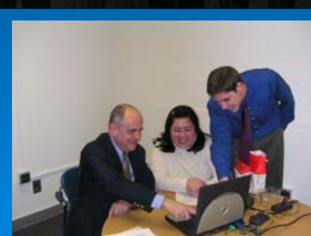


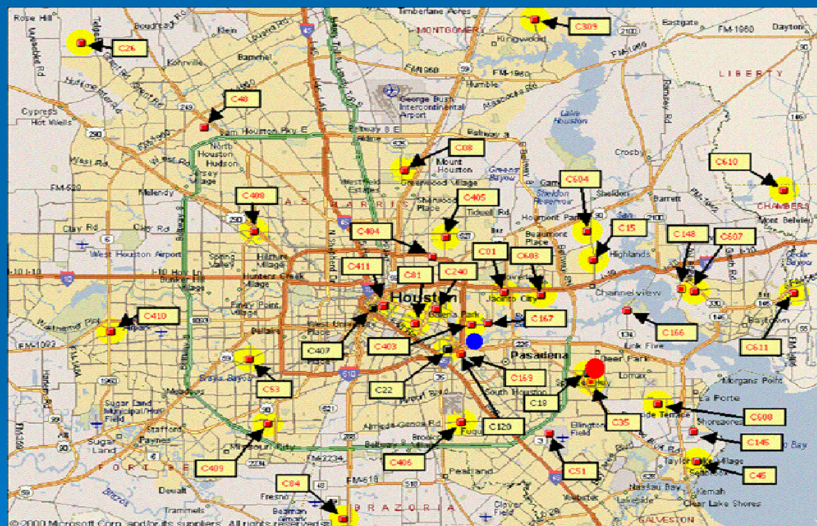




Current Projects

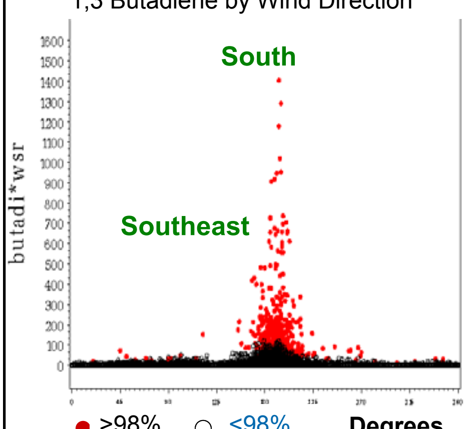
- Louise Camalier, Brendan Yoshimoto and Brian Sties, **"A Statistical Method to Corroborate Emission Inventories - Applied to Houston & Atlanta"**





Deer Park - Red
Clinton - Blue

1,3 Butadiene Upsets at Clinton



Ratio Mean Emission	Ratio Max Emission	Ratio Median AQ (98%)
0.02	0.13	0.02

Max Source	Max Quadrant (direction)
Low non-electric source	SE

•Double match!

Clinton Site

	A.Q. Median	E.I. 4x4	E.I. 8x8	E.I. 16x16	J.J. Approx.
Butadiene	.02	.016	.024	.025	.018
Propylene	.12	.019	.337	.202	.13
Ethylene	.17	.043	.086	.309	.14

Water Quality Trends in the Raleigh-Durham Metropolitan Area, 1980-2000.

- Ornella Darlington & Brian Currier
- Clients:
  - Dr. Barry Nussbaum
  - Ms. Ming Chang
  - Bryn Tracy, NC Division of Water Quality
  - Steve Kroeger, NC Div. of Water Quality

Rainfall Data (by Year)

The CORR Procedure

6 Variables: chapelhill durham ncstate raleigh rdu rougemount

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
chapelhill	33	3.88045	0.63446	128.05500	2.77500	5.10417
durham	33	3.95028	0.68651	130.35917	2.74167	5.37833
ncstate	33	3.83505	0.57727	126.55667	2.78833	5.11167
raleigh	33	3.82806	0.54406	126.32583	2.58000	4.97250
rdu	33	3.55917	0.53776	117.45250	2.80917	4.92833
rougemount	33	3.81641	0.56858	125.94167	2.83667	4.91417

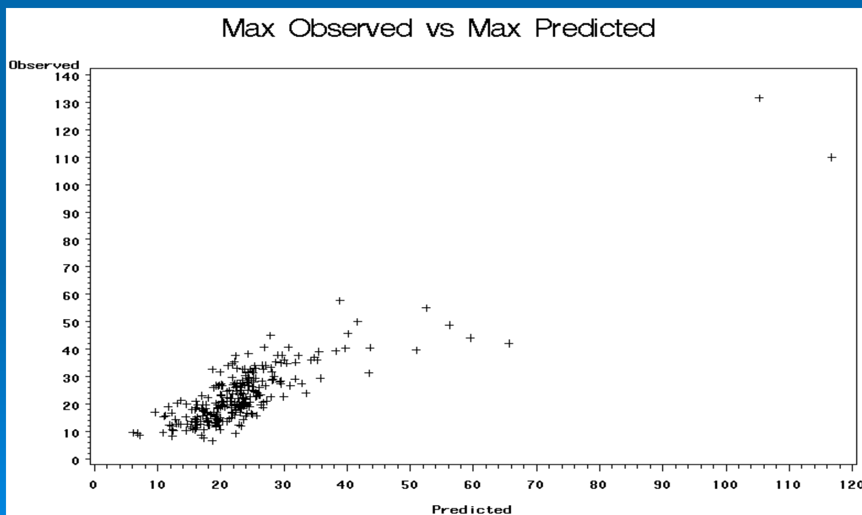
Pearson Correlation Coefficients, N = 33
Prob > |r| under H0: Rho=0

	chapelhill	durham	ncstate	raleigh	rdu	rougemount
chapelhill	1.00000	0.74621 <.0001	0.68399 <.0001	0.59842 0.0002	0.71450 <.0001	0.75855 <.0001
durham	0.74621 <.0001	1.00000	0.67341 <.0001	0.67487 <.0001	0.73360 <.0001	0.83255 <.0001
ncstate	0.68399 <.0001	0.67341 <.0001	1.00000	0.89141 <.0001	0.87491 <.0001	0.80740 <.0001
raleigh	0.59842 0.0002	0.67487 <.0001	0.89141 <.0001	1.00000	0.81616 <.0001	0.79113 <.0001
rdu	0.71450 <.0001	0.73360 <.0001	0.87491 <.0001	0.81616 <.0001	1.00000	0.78740 <.0001
rougemount	0.75855 <.0001	0.83255 <.0001	0.80740 <.0001	0.79113 <.0001	0.78740 <.0001	1.00000

Forecasting Fine Particulate Matter Air Pollution in Charlotte, NC

- Jennifer Lawhorn and Jamie Ridenhour
- Clients:
  - NCDENR/Air Division
    - Ms. Sheila Holeman
    - Mr. Mike Abraczinskas
    - Mr. George Bridgers

Winter Max Model: Observed vs. Predicted



Forecasted Exceedance of 15ug/m3

Charlotte Winter Model

	24 Hour Model	Daily Max Hour Model
Accuracy	81 %	82 %
False Alarm Rate	19 %	18 %
Critical Success Index	50 %	81 %
Probability of Detection	56 %	96 %

Testing Model Performance

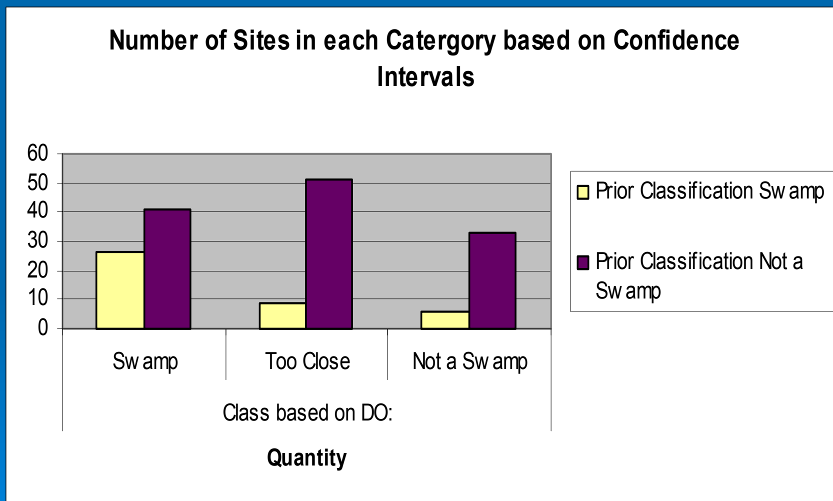
Charlotte Winter Model

		Forecasted Exceedance of 15 ug/m3			
		Daily 24 Model		Daily Max Hour Model	
Observed Exceedance Of 15 ug/m3		NO	YES	NO	YES
	NO	166	11	15	39
	YES	38	49	9	201

Is there a better way to define swamplands in the Coastal Plain and Sandhills?

- Audria Humes and Jera Mendenhall
- Client:
- Mr. Steve Kroeger, NCDENR/Water

Number of Sites in each Category based on Confidence Intervals



Other Student Accomplishments

- Five students graduated with a master's degree in statistics (Janet Bartz, Michael Crotty, Daric Harrington, Kristen Madsen and Tracy Robinson) and two are continuing on for a Ph.D. (Michael Crotty and Kristen Folley).
- Twelve students have gone onto graduate school programs in statistics. Gary Beecham, Ho Ling Cheng, Brian Copeland, Hugh Crews, Ronnie DeFrancis, Christy Finger, Amy Gabig, Paul Gallins, Douglas Hayden, Ben Ogorek, Kathy Woodside and Wendy Woolfolk.
- Four students are currently applying to graduate school: David Dail, Karen Donaghy, Valerie Harris and Alan Shoulders.
- Joseph McMichael, Lisa Cason, Andy Clarke, Angela Pitts, Jane Eslinger and Janet Bartz are employed at the Research Triangle Institute as environmental statisticians..
- Ten students have worked part-time at the U. S. Environmental Protection Agency as statisticians: Janet Bartz, Michael Crotty, Brian Copeland, Karen Donaghy, Shawn Edney, Daric Harrington, Sharon Isley, Kristen Madsen, Ben Ogorek and Kathy Woodside.

Conclusion

- Win-win-win situation for everyone.
- **Students win**
  - gain experience in doing research/consulting
  - writing reports
  - giving briefings
  - presenting papers
  - go on to graduate programs in statistics
  - go to work as environmental statisticians
- University wins
  - more students are pursuing graduate study
  - the faculty develops new contacts with environmental agencies
  - students are placed in rewarding careers

Conclusion Cont'd

- Clients win
  - because their data are analyzed
  - they can make more informed environmental policy decisions
  - they can hire the students for permanent or part time work
- SUMMARY
  - students have given 71 professional presentations and have written almost as many papers and reports.

The Future

- Implement program at Spelman College in Atlanta, GA.
- Find other interested partners.

Interlaboratory Validation of EPA Method 1668A: 209 Chlorinated Biphenyl Congeners by HRGC/HRMS

William A. Telliard
Director of Analytical Methods
U.S. EPA Office of Water
Office of Science and Technology

April 2004

Method 1668 – History

- **In early 1995, EPA EAD began development of an HRGC/HRMS method for determination of PCB congeners that the World Health Organization (WHO) determined as having dioxin-like toxicity**
  - Focused on 13 congeners listed in a 1994 WHO publication
  - Requested by EPA's Health Effects Research Laboratory (HERL) in RTP
  - HERL also requested that EAD test for other congeners

Method 1668 – History (continued)

- **First draft of EPA Method 1668 written in February 1995**
  - Based on EPA Method 1613 (CDDs/CDFs)
  - SPB-Octyl column selected based on work of George Frame, then at General Electric
  - Validated between February and September 1995 at Pacific Analytical Inc
  - First draft released upon request in October 1995
- **Method published in March 1997 (EPA-821-R-97-001)**

EPA Office of Water

PittCon 2004

Method 1668A – Background

- **In mid-1997, EPA began development of a method for determination of all 209 CB congeners**
  - Study plan written in September 1997
    - Find minimum number of solutions for separation of 209 congeners with a maximum valley height of 1 % between adjacent GC peaks – five solutions required
    - Establish solution concentrations inversely proportional to response – 3 concentrations required
    - Native congener solutions provided by AccuStandard
    - Select ^{13}C labeled internal standards such that the RRT for all congeners are in the range of 0.8 – 1.2

EPA Office of Water

PittCon 2004

Method 1668A – Single-lab Validation

- **Single-laboratory validation study conducted at Axys Analytical**
  - Single-lab validation study completed in mid-1999
  - Validation study report published in March of 2000.
    - Method details
      - SPB-Octyl and DB-1 column data
      - RTs, RRTs, ^{13}C RT, RRT, and quantitation references
    - Analysis of Aroclor 1221, 1232, 1016, 1242, and 1248

Method 1668A – Peer Review

- **Draft of Method 1668A released for peer review in September, 1999**
- **Peer review completed in November 1999**
  - Peer review sent to 21 organizations; 9 peer reviews returned.
  - Method 1668A revised based on comments received from peer reviewers
- **Method 1668A published in December 1999 (EPA-821-R-00-002)**

Method 1668A – Use Since 1999

- **EPA Studies**
  - National Fish Study – more than 700 samples
  - National Sewage Sludge (biosolids) Survey – 95 samples
- **TMDL Studies**
  - Delaware River Basin Commission
  - Ohio River Valley Water Sanitation Commission
  - State of New Mexico studies of the Gila, Dry Cimarron, and Upper Rio Grande

Revision of Method 1668A

- **Method 1668A revised in preparation for study**
  - References to IUPAC numbers deleted
  - Hexane deleted as extraction solvent for tissue to reduce loss of more volatile CBs – methylene chloride only
  - Note added to list suppliers of ^{13}C labeled compounds
  - Preservation temperature changed to <6 °C
  - Acid preservation eliminated
  - RTs and RRTs made "approximate"
- **Revision published with a date of August 20, 2003**

Plan for Interlaboratory Validation

- **Study Plan**
  - Drafted in February, 2003; published in May, 2003
  - Study Objectives
    - Characterize method performance in multiple laboratories and sample matrices
    - Evaluate and revise the QC acceptance criteria
    - Propose and promulgate a revision to Method 1668A at 40 CFR part 136

Study Plan (continued)

- **Study Requirements**
  - Each lab must follow the analytical and QC procedures in EPA Method 1668A
  - Deviations from Method 1668A require prior approval – no performance-based allowance for study
  - All data produced must be capable of independent verification
  - Each lab must have a comprehensive QC program in operation at the time of analysis of study samples

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Study Plan (continued)

- **Study Management**
  - Managed by the Statistics and Analytical Support Branch (SASB) in the Engineering and Analysis Division (EAD) of the Office of Science and Technology (OST) within the Office of Water (OW)
  - Day-to-day operations managed by the contractor-operated Sample Control Center at CSC under SASB guidance

Study Plan (continued)

- **Study Design**
  - Deviations from Method 1668A require prior approval – no performance-based allowance for study
  - All data produced must be capable of independent verification
  - Each lab must have a comprehensive QC program in operation at the time of analysis of study samples

Study Plan (continued)

- **Materials Provided**
  - Standards for calibration and spiking
  - Study samples
    - 2 wastewater samples
    - 2 biosolids (sewage sludge) samples
    - 2 tissue samples
- **Materials Supplied by Laboratories**
  - Reagent water for initial demonstration
  - Reagent water and playground sand/corn oil for blanks

Study Plan (continued)

- **Study Implementation**
  - Identify and select participant labs (SCC)
  - Collect, prepare, and ship standards and samples (SCC)
  - Analyze samples and report data (labs)
  - Review and assess data (EPA and SCC)
- **Laboratories Selected (14 total)**
  - 3 EPA Regional labs
  - 11 Commercial labs

Study Plan (continued)

- **Sample Identification and Collection**
  - Biosolids samples from excess from EPA's National Sewage Sludge Survey – composited to provide appropriate concentrations
  - Fish tissue samples from excess from EPA's National Study of Chemical Residues in Fish Tissues – composited to provide appropriate concentrations
  - Wastewater from a publicly owned treatment works (POTW) – spiked to provide appropriate concentrations
  - Each lab must have a comprehensive QC program in operation at the time of analysis of study samples

Detailed Instructions to Laboratories

- **Limited sample volume – not enough for re-extraction**
- **SPB-Octyl column must be used; data from alternate column(s) may be reported, if desired**
- **Suggested procedures for mixing and diluting analytical standards**
  - Instructions required because of limited volume of standards
  - 16 mixed/diluted solutions required, including 6 calibration solutions and 5 individual mix congener solutions

Suggested Analytical Sequence

- **Inject "A2" native congener mix solution**
  - Adjust GC conditions to meet the RTs in Table 2
  - Establish RRT and quantitation links
- **Separately inject the B2, C2, D2 and E2 solutions**
  - Establish RRT and quantitation links
- **Inject the 209 congener solution**
  - Establish RRT and quantitation links for co-eluted congeners

Suggested Analytical Sequence (continued)

- **Inject 5- or 6-point cal solutions CS-0.1 – CS-5**
  - Number of points dependent on vintage of instrument
  - Determine average RFs and RRs
- **Inject 209 congener solution**
  - Update RTs and RRTs for all congeners and congener groups
  - Update RFs for natives without a labeled analog
- **[- Presumed break in sequence to allow for reduction of calibration data -]**

Suggested Analytical Sequence (continued)

- **Verify calibration**
  - Will allow analyses of all samples and blanks in 12-hour period
    - CS-3 calibration solution
    - 209 congener solution
- **Analyses**
  - Reagent water blank
  - Reagent water lab control sample (OPR) #1 (Study sample #1)
  - Reagent water lab control sample (OPR) #2 (Study sample #2)

Suggested Analytical Sequence (continued)

- **Analyses (continued)**
  - Wastewater sample #1 (Study sample #3)
  - Wastewater sample #2 (Study sample #4)
  - Solids/tissue blank (playground sand/corn oil)
  - Tissue sample #1 (Study sample #5)
  - Tissue sample #2 (Study sample #6)
  - Biosolids sample #1 (Study sample #7)
  - Biosolids sample #2 (Study sample #8)
- **Sequence end**

Study Limitations

- **MDL and initial demonstration (IPR) not required**
  - Large resources to conduct MDL and IPR studies
  - Volunteer labs
  - If MDL and/or IPR data received, EPA will consider
- **Spikes at multiple concentrations not necessary**
  - Congeners are distributed across the analytical range in tissue and biosolids samples; wastewaters are spiked with Aroclor(s)
- **Matrices tested in study are representative**
  - Additional matrices could have been included if external funding had been available

Study Schedule

- **Study plan published May 2003**
- **Revised method published August 2003**
- **Participant laboratories selected September 2003**
- **Sample preparation**
  - Sample matrices shipped to prep lab October 7, 2003
  - Instructions sent to prep lab October 23, 2003

Study Schedule (continued)

- Reporting requirements and forms sent to participant labs November 13, 2003
- Analytical standards shipped to participant laboratories November 18, 2003
- Results of analyses of test samples by sample prep lab sent to SCC November 21, 2003
- Samples shipped November 24, 2003

Study Schedule (continued)

- Results requested by January 1, 2004
- Due date for results extended to February 1, 2004 in a conference call in December, 2003
- As of March 3, 2004, data had been received from 4 labs
  - 3 electronic
  - 1 hardcopy
- Data will be reduced and a report made available after data are received

Summary of Narratives from 4 Labs

- **Two labs had difficulty extracting biosolid samples**
  - Problem overcome in one lab by diluting the extracts and carbon cleanup
  - In second lab, extracts contained white crystals that could not be removed
- **One lab had difficulty extracting fish-tissue samples**
- **One lab reported low recoveries for some labeled CBs in all samples**
- **One lab reported GC column stability problems**
- **One lab used layered acid and base silica plus alumina for cleanup of wastewater sample**
- **Other problems reported appeared to be minor**

Additional Information

- **For additional information contact:**

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EPA WET Center: A New Tool to Support the Quality of the Clean Water Act's Whole Effluent Toxicity NPDES Program

Marion Kelly
U.S. Environmental Protection Agency
April 2004

Presentation Overview

- What is WET testing and how does it work?
- Why do we care? (i.e., why do we need a Technical Support Center)
- Technical Support Center purpose
- Organizational structure

What is WET testing

- Whole Effluent Toxicity (WET) – Defined as the aggregate toxic effect of an effluent measured directly by an aquatic toxicity test
- WET tests – Lab experiments designed to measure the biological effect of effluents on freshwater and marine organisms. May be:
  - Acute or Chronic
  - Fish, Invertebrate, Plants
- EPA WET Test Methods – a suite of aquatic toxicity test methods designed specifically for measuring acute and chronic toxicity and promulgated for use in NPDES permitting programs.

How does it work?

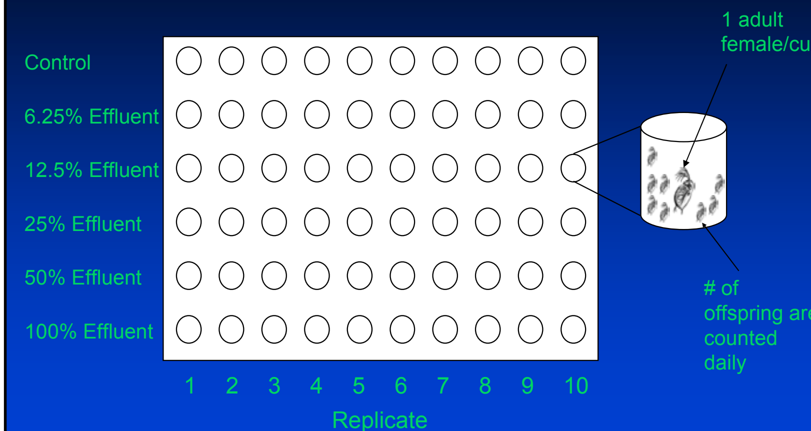
- Groups of organisms of a designated species (e.g., fathead minnow)
- Depending on purpose of the test, the sample could be an effluent, a receiving water, or reference toxicant
- Observations are made at predetermined exposure periods
- At end of test, responses of the test organisms are used to estimate the effects of the toxicant or effluent

Example WET Test Method

- Cladoceran, *Ceriodaphnia dubia*, Survival and Reproduction Test

- Test Treatments
  - Organisms are exposed to a range of 5 effluent concentrations and a control
- Replicates
  - 10 organisms are exposed to each treatment
- Biological Measurements
  - Survival and reproduction are measured for 7 days

Example WET Test Design



Example WET Test Data

Reproduction (# of offspring)

	1	2	3	4	5	6	7	8	9	10	Average
Control	26	7	25	24	23	26	30	24	28	26	23.9
6.25%	24	26	21	29	23	20	24	25	27	18	23.7
12.5%	18	25	27	20	17	19	24	20	17	19	20.6
25%	19	25	24	13	24	18	16	17	18	24	19.8
50%	0	17	12	0	5	9	13	0	16	0	7.2*
100%	0	0	0	0	0	0	0	0	0	0	0.0*

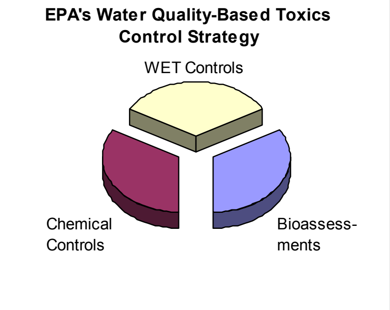
- Each treatment is statistically compared to the control to determine toxicity

- In this example: the effluent is toxic at >25% dilution

* Average is significantly different from the control at the 95% confidence level

Why do we care?

- As part of the Clean Water Act, EPA has been mandated the responsibility of controlling “toxic pollutants in toxic amounts.”
- Toxicity testing is the <u>only way</u> to monitor the toxic effects of effluents on living organisms
- Whole effluent toxicity tests <u>integrate</u> the effects of multiple toxics in complex matrices
- WET is one of three components of EPA’s integrated approach to water quality based toxics control



Why do we care? (continued)

- These 3 components are complementary (each with individual advantages and limitations) and when implemented collectively, they provide the most complete approach to controlling "toxic pollutants in toxic amounts."
- WET implementation technical questions/issues raised by permitting authorities and/or regulated community are addressed.
- Appropriate WET implementation requires good science, defensible data, and national program consistency.

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External Assessments of EPA WET Test Methods

- *"Existing WET testing methods are technically sound, but EPA should develop a more effective approach for promoting and monitoring national consistency in implementation of the WET program."*
  - SETAC Pellston Proceedings
  - WERF Regulatory and POTW Survey

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Consistency Issues

Permit requirements for the same outfall discharge in two jurisdictions may differ greatly:

State/ Region A	State/ Region B
Two freshwater species	Three saltwater species
Automatic WET limits	No WET limits
WET limits (for lethal effects only)	WET limits (for both lethal and sub-lethal effects)
Test frequency once per five years	Test frequency once per month
24-Hour LC_{50} Test	7-Day chronic NOEC or IC_{25} test
Allow use of CO_2 cap for NH_3	No allowance for CO_2 cap

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Ability to Assist With TRE/TIE Technical Issues

TRE = Toxicity reduction evaluation

TIE = Toxicity identification evaluation

Specific TRE/TIE Success Stories

- Linden Roselle Sewerage Authority, NJ
- Clark Petroleum, TX
- San Francisco Bay Area POTWs

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POTW TRE/TIE Success Story
Linden Roselle Sewerage Authority, NJ

- Issue
  - Primary ammonia toxicity reduced through pretreatment limits
  - Secondary causes complex, highly variable
- TRE Elements
  - Facility performance evaluation
  - TIE
  - Toxicity source evaluation
- Results
  - In 1997, major ammonia source was eliminated
  - Reduction in toxicity to compliance levels

Industry TRE/TIE Success Story
Clark Petroleum, TX

- Issue
  - Toxicity to *Mysidopsis bahia*
  - Intermittent toxicity
- TRE Elements
  - Accelerated WET testing
  - Facility performance evaluation
  - Toxicity source evaluation, including TIEs
- Results
  - Excess fluoride identified as the toxicant
  - Fluoride streams re-routed off industrial site and recycled into synthetic fluorspar

Watershed TRE/TIE Success Stories
San Francisco Bay Area POTWs

- Issue
  - Consistently detected acute toxicity
- TRE Elements
  - TIE showed diazinon and chlorpyrifos
  - Monitoring studies showed large differences in loading and removal among POTWs
  - Source identification showed most loading was residential
- Results
  - Substantial removal of insecticides from influent wastewater
  - Ongoing effort to identify and control sources, identify removal processes and operations
  - Multifaceted public awareness program

Other issues where there are significant differences between jurisdictions

- TRE/TIE technical issues
- Interpretation of WET test results, including anomalous data sets, PMSD, etc.

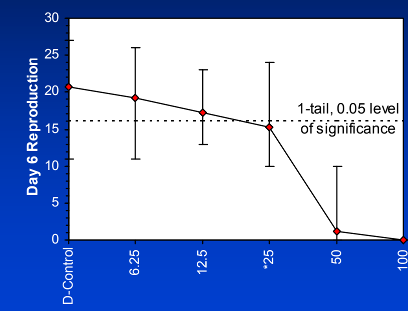
Interpretation of WET test results, including anomalous data sets, PMSD, etc.

Sample Data Sets

Sample Test Data Set #1

Sample Test Data Set #1 - *Ceriodaphnia dubia* Survival and Reproduction Test

Survival NOEC	25
LC50	40.613
Reproduction NOEC	12.5
Reproduction IC25	22.969



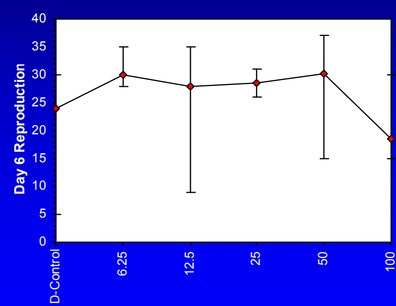
Sample Test Data Set #2

Requires use of concentration-response guidance

Sample Test Data Set #2 - *Ceriodaphnia dubia* Survival and Reproduction Test

Survival NOEC	100
LC50	>100
Reproduction NOEC	100
Reproduction IC25	>100*

* IC25 calculated as 86.82, but based on concentration-response evaluation, this result was determined to be anomalous and IC25 reported as >100



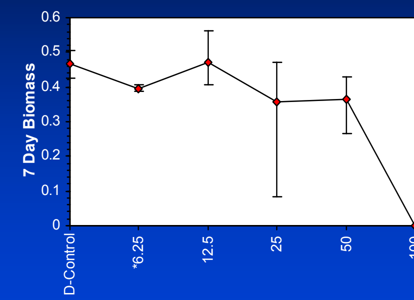
Sample Test Data Set #3

Requires use of concentration-response guidance

Sample Test Data Set #3 - Fathead Minnow Larval Survival and Growth Test

Survival NOEC	50
LC50	51.404
Growth NOEC	50*
Growth IC25	51.446

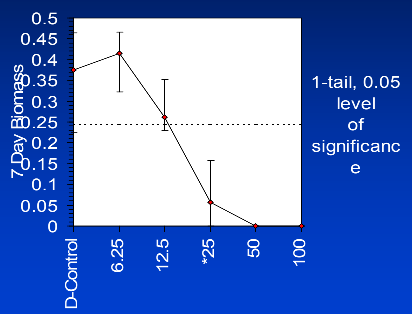
* 6.25% treatment was significantly different from control, but based on concentration-response evaluation, this treatment was determined to be anomalous and NOEC reported as highest concentration not significantly different from the control



Sample Test Data Set #4

Sample Test Data Set #4 - Fathead Minnow Larval Survival and Grov

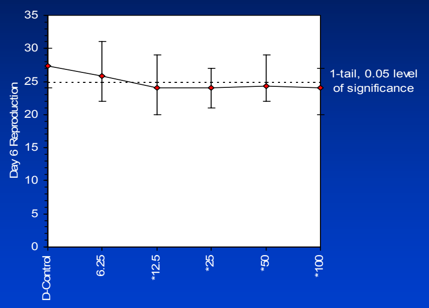
Survival NOEC 12.5
LC50 19.9
Growth NOEC retest*
Growth IC25 10.9
* The test PMSD was 35% and exceeded the upper PMSD criteria of 30%, so the



Sample Test Data Set#5

Sample Test Data Set #5 - *Ceriodaphnia dubia* Survival and Reproduction Test

Survival NOEC 100
LC50 >100
Reproduction NOEC 100*
Reproduction IC25 >100
*** Reproduction NOEC was calculated as 6.25%, but PMSD was 8.7% and below lower PMSD bound of 13%. Effect levels at each concentration were less than 13%,**



What will the WET TSC do?

- Serve as a national review body, providing recommendations and guidance on hard-to-resolve WET technical issues.
- Provide technical support to states and EPA Regions to address complex WET issues.
- Provide a means by which EPA could ensure that a core group of staff exists with the technical expertise needed to address complex issues surrounding both case-specific and more general WET testing issues.

Why create a WET TSC?

- EPA and many states face an increasing level of permit challenge sophistication.
- EPA and states also are losing staff with historical institutional and technical knowledge of complex programs such as the WET testing program.
- Centralized center will help address both problems by providing technical and programmatic expertise, institutional knowledge.
- Center also will ensure consistency of state and Regional responses to similar technical issues arising in different locations or situations.

Why create a WET TSC? (continued)

- Serve as an outreach center and clearinghouse for consistent and correct responses to WET implementation questions, including those involving NPDES permit challenges
- Provide an expert support center to address the need for WET expertise and training of permit authorities due to staff turnover
- Provide a National Consistency Coordination Center for EPA Regions and NPDES States on WET implementation approaches

Common-Sense Approach to Data Interpretation: Experience from EPA's Effluent Guidelines Program

William A. Telliard, Director
Analytical Methods
Office of Science & Technology
Office of Water

"Any fool who analyzes a sample more than once gets exactly what he deserves."

Data Review

Office of Water

Goals for Data Review

- Ensure that data used are scientifically sound and legally defensible.
- Make certain that the data user fully comprehends the purpose for the data collection and the impacts of the approach and methods selected.
  - Including understanding of any data qualifiers used.
- Ensure that achievement of the data quality objectives can be fully ascertained from the data review process.

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Data Review Scope and Philosophy

- The data review process is applied to all data types, but customized per method, study, and regulatory requirements.
- The general philosophy should be to include as much useful data as possible (i.e., data with QC failures are not excluded unless the failure is extreme and/or in combination with other data quality issues).
- The final decision on data usability is left to the decision maker or data user.

Data Review for Chemical and Microbiological Methods

- Data review is a standardized multi-step process designed to provide a comprehensive, timely assessment of data quality and, if need be, contractual compliance.
- This process begins with a review of summary level data (standard forms) from the laboratory

Data Review for Chemical and Microbiological Methods (cont.)

- The need to review all raw data (bench sheets, calculations, instrument printouts, etc.) will depend on the type of analysis and the nature of the data produced, in particular:
  - Many chemical methods involve automation and instrument data systems, so spot checks of data and calculations may suffice.
  - In contrast, microbiological methods are generally performed manually and, instrument printouts are not available. As a result, ***all*** raw data for microbiological analyses must be scrutinized closely and ***all*** calculations verified.

The Data Review Process

- **Data Completeness Check:** Confirms that all requested analyses were performed, and all deliverables were submitted.
- **Instrument Performance Check:** Verifies that multi-point calibrations, calibration verifications, and calibration blanks were analyzed at the appropriate frequency and met method and contract specifications.

The Data Review Process (cont.)

- **Laboratory Performance Check:** Verifies that the laboratory performed the analytical procedures correctly with an acceptable level of precision and accuracy.
  - Items evaluated may include holding times, initial and ongoing precision and accuracy tests, preparation blanks, standards, media sterility checks, positive/negative control results, incubation length, and incubation temperature.
- **Method/Matrix Performance Check:** Helps discern whether QC failures are associated with lab or method performance vs. matrix complexities. Evaluates recoveries of spikes and verifies that the appropriate sample dilutions and cleanups were performed.

The Data Review Process (cont.)

- **Assessment of Data Quality and Usability:** Overall assessment of the data based upon the findings of the steps above.
  - Can be expressed in a written data review narrative that summarizes all data failures and resulting qualifications of data.
  - Can add qualifiers directly to the database or electronic data file (MS Excel spreadsheet, dBase file, etc.).

What should and should not be evaluated in the data review process?

- At a minimum, summary level data review should be performed.
- If resources are available, QC summary level data should be reviewed for chemical methods.
- Raw data (bench sheets, instrument printouts, etc.) for chemical methods may be only spot checked, and may not need to be evaluated in detail.

What should and should not be evaluated in the data review process? (cont.)

- If trip, field, or equipment blanks are provided, these field QC results should be reviewed.
- For microbiological methods, raw data must be closely scrutinized and all calculations verified.

Automated Data Review

- The electronic output from today's instrumentation makes it possible for the data to be reviewed using automatic processes.
- EAD has automated its data review processes for metals, organics, PCBs, dioxins/furans, and pesticides/herbicides.
- Automated review significantly reduces data review time and increases accuracy and consistency of the data review process.

Example Automated Data Review Report

Microsoft Access - [CAL]

File Edit View Tools Window Help Ditto Ditto10X

100% Close

LIST of CAL+VER SAMPLES

Blank = HOMOB

Sample	Analyte	Amount	Det. Limit	Spike Conc.	% Diff.	Method	Anal. Date	Anal. Hour	Anal. Min.	Batch ID
VER1	1,2,3,4,6,7,8-HpCDD	49.6	0	50	99.20%	1613B	12/10/2000	18	49	
VER2	1,2,3,4,6,7,8-HpCDD	49.6	0	50	99.20%	1613B	12/11/2000	7	40	
Sample	**Analyte**	**Amount**	**Det. Limit**	**Spike Conc.**	**% Diff.**	**Method**	**Anal. Date**	**Anal. Hour**	**Anal. Min.**	**Batch ID**
VER1	1,2,3,4,6,7,8-HpCDF	50.1	0	50	100.20%	1613B	12/10/2000	18	49	
VER2	1,2,3,4,6,7,8-HpCDF	50.8	0	50	101.60%	1613B	12/11/2000	7	40	
Sample	**Analyte**	**Amount**	**Det. Limit**	**Spike Conc.**	**% Diff.**	**Method**	**Anal. Date**	**Anal. Hour**	**Anal. Min.**	**Batch ID**
VER1	1,2,3,4,7,8,9-HpCDF	48.9	0	50	97.80%	1613B	12/10/2000	18	49	
VER2	1,2,3,4,7,8,9-HpCDF	49.2	0	50	98.40%	1613B	12/11/2000	7	40	
Sample	**Analyte**	**Amount**	**Det. Limit**	**Spike Conc.**	**% Diff.**	**Method**	**Anal. Date**	**Anal. Hour**	**Anal. Min.**	**Batch ID**
VER1	1,2,3,4,7,8-HxCDD	49.2	0	50	98.40%	1613B	12/10/2000	18	49	
VER2	1,2,3,4,7,8-HxCDD	48	0	50	96.00%	1613B	12/11/2000	7	40	
Sample	**Analyte**	**Amount**	**Det. Limit**	**Spike Conc.**	**% Diff.**	**Method**	**Anal. Date**	**Anal. Hour**	**Anal. Min.**	**Batch ID**
VER1	1,2,3,4,7,8-HxCDF	50.7	0	50	101.40%	1613B	12/10/2000	18	49	
VER2	1,2,3,4,7,8-HxCDF	49.6	0	50	99.20%	1613B	12/11/2000	7	40	
Sample	**Analyte**	**Amount**	**Det. Limit**	**Spike Conc.**	**% Diff.**	**Method**	**Anal. Date**	**Anal. Hour**	**Anal. Min.**	**Batch ID**
VER1	1,2,3,6,7,8-HxCDD	49.7	0	50	99.40%	1613B	12/10/2000	18	49	
VER2	1,2,3,6,7,8-HxCDD	48.6	0	50	97.20%	1613B	12/11/2000	7	40	
Sample	**Analyte**	**Amount**	**Det. Limit**	**Spike Conc.**	**% Diff.**	**Method**	**Anal. Date**	**Anal. Hour**	**Anal. Min.**	**Batch ID**
VER1	1,2,3,6,7,8-HxCDF	49.4	0	50	98.80%	1613B	12/10/2000	18	49	
VER2	1,2,3,6,7,8-HxCDF	49.6	0	50	99.20%	1613B	12/11/2000	7	40	

Page: 1

Use of Data Qualifiers

- Data qualifiers are generally program-specific (e.g., CLP, effluent guidelines)
- Serve to advise the data user of issues associated with specific sample results.
- Not meant to exclude the data (just a warning)

Examples of Data Qualifiers Used in the Effluent Guidelines Program

Qualifier	Meaning	Example Reasons
Acceptable quality, but may be a minimum value	Result may be biased low	MS, surrogate, CV or OPR % recovery below criteria
Acceptable quality, but may be a maximum value	Result may be biased high	MS, surrogate, CV or OPR % recovery above criteria
Estimated Value	Result bias (high vs. low) cannot be determined	Holding time exceeded, MS/MSD RPD exceeded criteria
Less than "<" or greater than ">"	Numerical value exceeded the calibration range	Laboratory did not perform appropriate dilutions
Exclude	Not acceptable for use	Gross QC failures; compound identification questionable

Review Procedures for Whole Effluent Toxicity Test Data

- Review of reference toxicant control charts.
- Evaluation of within-lab variability and comparison to national performance.
- Evaluation of results beyond control limits.
- Review of concentration-response patterns.
- Evaluation of the concentration range.
- Comparison hypothesis testing endpoints and point estimates.

When should additional data review be performed?

- If anomalies or issues are encountered in the statistical and engineering review.
- If the regulation of a particular treatment technology or certain target analytes are known to be contentious.
- If data will be used to derive the final regulatory list and limitations, additional reviews are often warranted to head off stakeholder challenges.

When should I suspect possible laboratory fraud?

- When raw data do not support the results reported by the laboratory, e. g.,
  - raw data shows an OPR standard was analyzed a week prior to the samples being analyzed, but
  - summary data shows the OPR standard was analyzed at the same time as the field samples.
- When there is a large number of hand-corrected data.
- If there is an illogical sequence of dates.
- If there are never any indications of QC failures, re-extractions, etc.

Actions if Laboratory Fraud is Suspected

- Re-check the data to be sure that your suspicions are supported.
- Notify the program official responsible for the data.
  - May request additional data from the permittee to resolve the issue.

Engineering and Chemical Process Reviews

- **Wastewater Characterization** – Identification of conventional, non-conventional, and toxic pollutants of interest in each industry's wastewaters.
- **Effluent Limitations Development** – Document pollutant levels in the industry's discharges along with the associated pollutant variability.
- **Control and Treatment Technology** – Identification of pollutant reduction efficiencies in various in-plant and end-of-pipe control technologies used by industries.